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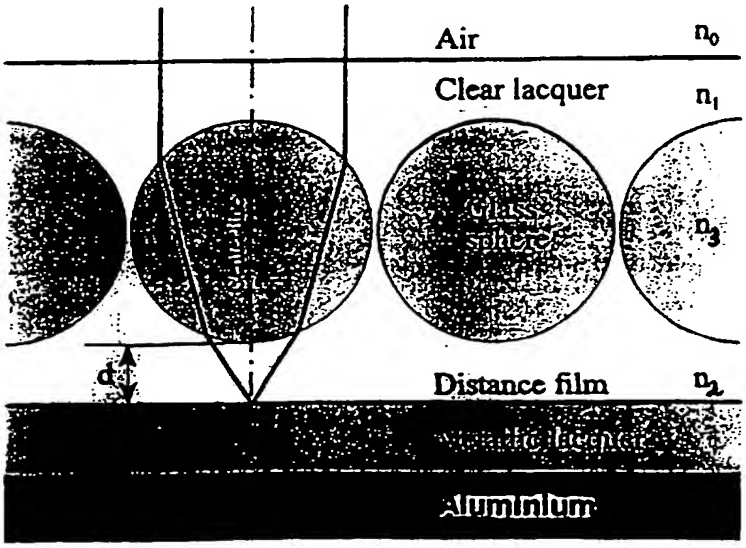
(54) Title: RETRO-REFLECTING SHEET MATERIAL AND METHOD OF PREPARING SUCH MATERIAL



(57) Abstract

The invention relates to a new retro-reflecting sheet material comprising a substrate having a retro-reflective surface, where said retro-reflective surface comprises several layers including a mono layer of spherical beads and possibly one or more transparent layers. Further, the invention relates to a new method of preparing said retro-reflective surface on a substrate comprising providing said layers on the substrate. The layers constituting the retro-reflecting sheet material are applied one by one to the substrate substantially by rollers, and preferably by means of coil coating.

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Retro-reflecting sheet material and method of preparing such material

The invention relates to a new retro-reflecting sheet material comprising a substrate having a retro-reflective surface, where said retro-reflective surface comprises several layers including a mono layer of spherical beads and possibly one or more transparent layers. Further, the invention relates to a new method of preparing said retro-reflective surface on a substrate comprising providing said layers on the substrate.

The retro-reflective sheet materials provided by the present invention are useful as road signs, automobile licence plates and the like.

Retro-reflective sheet material is previously known from European Patent Specification having publication No. 9253. EP-9253 discloses a retro-reflective surface on a sheet material of metal prepared by passing the sheet material which is provided with a layer of transparent material whereto a mono layer of glass beads is adhered, through a sheet rolling mill and applying a further layer of transparent material over said glass beads. Pressure is applied to the beads via a platen overlying said beads when rolling through the mill.

Providing a retro-reflective sheet material according to EP-9253 includes a quite complicated and time consuming process resulting in a rather expensive product. In addition to applying several layers of transparent material to a substrate, glass beads are adhered thereto by dropping a copious quantity of beads to a thin adhesive coating and shaking off those which do not adhere, and furthermore the substrate provided by a mono layer of glass beads are covered by a platen and passed through a sheet rolling mill to cause the beads to indent the surface of the substrate. To succeed in indenting the beads into the surface of the substrate, the material of the substrate should

preferably be rather soft. Furthermore, this process involves difficulties in controlling the beads to indent correctly into the transparent layer and the substrate.

It is an object of the invention to provide a retro-reflective sheet material having proper retro-reflective properties in an efficient way involving excellent process control.

This object is achieved by providing a retro-reflecting sheet material wherein the retro-reflective surface further comprises a layer of light reflecting material, and wherein substantially all the layers constituting said retro-reflective surface have been applied to the substrate by rollers.

It is a further object of the invention to apply a retro-reflective surface to a sheet material by primarily using rollers.

This object is achieved by preparing a retro-reflective surface wherein the layers are applied one by one to the substrate substantially by rollers, and between every applying by roller of a new layer curing and cooling are performed in a mainly conventional way.

These and further objects of the invention are obtained in accordance with the features defined in the independent claims 1 and 8, and dependent claims 2-7 and 9-15.

The invention will now be further described by means of examples and with reference to the drawings in which:

Fig. 1 is a schematic depiction of the light retro-reflecting sheet material according to the invention.

Fig. 2 is a schematic depiction of another alternative embodiment of a retro-reflecting sheet material according to the invention.

Fig. 3 shows the relative intensity value of the retro-reflectivity of samples according to a first example with a light entrance angle β of 5°.

Fig. 4 shows the same as in Fig. 3, but with a light entrance angel β of 30°.

Fig. 5 and 6 shows the same as in Fig. 3 and 4 respectively, but with samples according to another, second example.

The substrate can be any material capable for roller application. The substrate is usually of metallic materials such as steel or aluminium suitable for road signs, automobile licence plates and the like. Preferably the substrate is an aluminium sheet material or aluminium alloy sheet material. However, for other purposes the substrate can be made of other suitable sheet materials like paper, textile or plastic.

The substrate might be embossed such that small indentations are present at the substrate surface. This can be done by rolling the substrate through a roller mill where the roller is having spikes constituting negatives to the indentations being made in the substrate.

To obtain a retro-reflective sheet material according to the present invention a layer of light reflecting material at the bottom of the retro-reflective surface on the substrate is necessary. Such light reflecting material can be a metallic surface on the substrate itself, a metallic foil, or preferably a metallic coating. Clear transparent coating might be applied when the substrate is embossed to give half spheres serving as retro-reflective elements or metallic used where metallic flakes provide the reflective properties. This metallic coating can be further improved by half-spheres embossing to give better angular retro-reflective properties. A typical metallic coating comprises resin, aluminium flakes, crosslinker, catalyst, solvent and flow additive. The metallic coating is applied to the substrate by using rollers, i.e. the metal strip running between coating rollers which apply the wet coating film upon the strip surface. Preferably the application of metallic coating is performed by means of coil coating, i.e. continuously application of a coating solution/dispersion on a metallic strip, on one or both sides, using a single or multiple roll configuration coater, utilising forward and reverse coating modes, followed by continuous curing in conventional ovens, cooling and further processing.

A transparent layer can be applied on top of the light reflecting layer. Such transparent layers comprise clear transparent and smooth lacquers and is typically a polymer coating comprising resin, solvents, crosslinker, catalyst and flow additive. The polymer coating might contain a transparent pigment, opaque beads or dye like for instance

phtalocyanine blue, phtalocyanine green or tetrachloroisoindoline yellow, in order to impart a colour to the retro-reflective surface. A transparent layer is not strictly necessary for obtaining a retro-reflective sheet material according to present invention. However, it might be desirable to apply a transparent layer and in this way obtaining a spacing distance layer between substrate and spherical beads which is necessary to achieve maximum retro-reflective properties. Such layers can be applied by using rollers or preferably by means of coil coating as explained above.

On top of the light reflecting layer or if applied, on top of the transparent layer, a mono layer of spherical beads is applied. Such spherical beads might be transparent glass beads preferably having a refractive index of 1,5 -2,5, for instance of the type SWARCO high index 2,1 40-80 μm particle size diameter. The refractive index and size of the beads affect the optimum distance that the beads should be spaced from the reflector; i.e. smaller beads and higher refractive indices require smaller optimum spacing from the substrate. The relation between the refractive index and the spacing distance layer can be expressed by the following formula: $d = \frac{r}{1 + \frac{n_1 n_3}{n_3 n_2 - 2 n_1 n_2}}$

d defines the spacing distance layer, and the different n's define the refractive indices as shown in the attached figures Fig. 1 and 2. In Fig. 1 a schematic description of a retro-reflecting sheet material where spherical glass particles partly sunk in a spacing distance layer separating the spheres from the metallic lacquer and having a transparent lacquer above the spheres, is shown. In Fig 2 a schematic description of a retro-reflecting sheet material where the spacing distance layer forms a shell around each sphere and the spheres are further partly sunk in the metallic layer, is shown. A transparent layer is applied above the layer of spheres.

The spherical beads are dispersed in a polymer coating, and the dispersion is applied to the substrate which already may comprise one or two other layers, by using rollers as explained above. The dispersion typically comprise resin, solvent, crosslinker, catalyst, spherical beads and anti-settling agent. Preferably said dispersion is applied by means of coil coating as explained above.

Each spherical bead constituting the above said mono layer may be coated in advance by a polymer coating and/or subsequently by a light reflecting material like for instance a

metallic coating. Thus, coated spherical beads will have a shell acting as a spacer to provide relevant optical properties for each spherical bead.

A polymeric coating of above the described character applied on the spherical beads is preferred because the important distance between the spherical bead and the reflective element is thereby better defined. It is a well known problem to achieve a homogeneous defined and consistent coating onto a small spherical particle. This is particularly so when dimensions of the particle are of the same magnitude as the coating layer, e.g. a homogeneous evenly distributed coating of 30 μm thickness onto a particle with mean radius of 35 μm is relatively difficult to obtain. To achieve a polymeric coating in an economic way this invention uses spray drying techniques, fluidized bed techniques, or preferably a combination of the two said techniques. Spray drying is effective but unfortunately suffers from poor layer thickness consistency and agglomeration. This leads to a process difficult to control. Fluidized bed technology is also effective but suffers from basically the same drawbacks as spray drying. Preferably a coating technique of combined fluidized bed and spray drying is used. This combination does not suffer from above mentioned drawbacks.

This technique is further described in the applicant's own patent application; "Spherical beads for light retro-reflective applications and method of preparing such beads", filed as a PCT application on the same day as the present application.

When using spherical beads that are coated with a light reflecting material in advance of making the mono layer of spherical beads, the light reflecting material on the upper surface of the applied mono layer must be removed. The light reflecting material might thus be partly removed mechanically, chemically or thermally. This results in a mono layer of spherical beads having a light reflecting material at the parts turning towards the substrate and not at the parts now making the upper surface of the substrate. In this way a light reflecting layer is applied to the substrate. Thus, a light reflecting layer between the substrate and the mono layer of spherical beads can be alternatively provided in this way.

On top of the mono layer of spherical beads a transparent layer can be applied. This is strictly not necessary. Such transparent layer can be applied by using rollers or

preferably by means of coil coating and if so the transparent layer is made by a polymer coating, or it might be applied by means of foil or powder coating. Polymer coatings like those defined above are useful also for this purpose. Said transparent layer is smooth and is intended to provide satisfactory surface properties to the finished product . It might be coloured and may consist of several layers. Also a polymeric foil laminate or powder coating to the layer of spherical beads can be employed as a top layer.

Above described clear lacquers and metallics used in this invention as base coating, distance layer, and top coats can be composed of different film forming polymers and/or dispersion.

Applicable polymer solutions are polyesters, polyurethane's, acrylics, epoxies, phenolics, polycarbonates, fluorocarbons etc. where the polymeric backbone can be functional to give thermosetting or thermoplastics properties.

Polymer dispersions and the like, related close to the solution products may be used and are usually but not necessary water based or water carried. These can be composed of the same polymeric compounds described above.

The invention will be further explained by examples and attached figures.

Example 1 and 2 are laboratory prepared in a way that closely simulates the conditions present at full scale coil coating production.

Example 1

Several samples of retro-reflecting materials were prepared by applying two layers of light reflectors upon mill finished aluminium alloy panels and also hot AC pretreated.

The aluminium substrate sheet was first coated with a dry film thickness (DFT) of 14 µm layer of a metallic coating containing N-alkyd Z 2933 (PE-uvð), Stapa Metallux 212, DBE-ester, Desmondur™ BL 3175, Cuprisec™ Zink 12%, cured at about 225°C, upon which a mono layer of about 60-70 µm DFT of SWARCO high index 1,9 glass beads dispersion was applied.

The samples have been subject to weathering, corrosion, temperature, water and chemicals resistance tests, according to ISO 7591 and ASTM B117, in order to study the impact of the mentioned tests on the retro-reflective properties. The relative intensity values of the retro-reflectivity, measured by an observation angle of 0°20' and an entrance angle ß of 5° respectively 30° are given in Fig. 3 and Fig. 4, respectively.

Tests definition :
t1 - temperature resistance
t2 - QUV B resistance
t3 - QUV A resistance
t4 - humidity resistance
t5 - water resistance
t6 - cleanability
t7 - resistance to fuel
t8 - resistance to saline mist.

The product of this example showed excellent reflective properties in both angles of light incidence. These reflective properties do not diminish under the level stated by ISO 7591 when samples of the product are submitted to various tests, as mentioned above.

Example 2

Retro-reflective samples were produced in the same way as before in Example 1 successive with coating 4 layers on the aluminium alloy substrate which was of mill finished quality and hot AC pretreated.

The first layer, having DFT of about 14 µm is a metallic coating as described above, upon which a transparent Lumiflon LF 552 layer is applied of DFT 5 µm. The third coating layer is the glass beads dispersion of DFT 70-100 µm, as explained in Example 1. A forth 12 µm layer of a transparent fluoropolymer lacquer was applied on top of the glass beads mono-layer.

The variation of the retro-reflective characteristics when the samples of this retro-reflective surface are subject to the tests mentioned in Example 1 is shown in Fig. 5 and Fig. 6, respectively.

All the samples of the product described in Example 2 showed much higher retro-reflectivity then the minimum accepted value stated in ISO 7591. As shown in Fig. 3 and 4 the retro-reflective properties are not negatively affected by changing the light entrance angle, or by carrying out wheathering/corrosion tests.

Example 3

In a full scale coil coating roller application a dispersion of glass beads was applied on an aluminium substrate.

A composition of the following ingredients was applied onto aluminium substrate giving a uniform mono-layer of glass beads:

Fluorocopolymer (LF 552) (40% solids)	100,0 g
High index glass beads (Swarco 2.1)	225,0 g
Isocyanate (Desmodur BL 3175)	8, 0 g
Curing catalyst (Cuprisec Zink 12%)	0,8 g
Solvent (DBE Dibasic Ester)	18,0 g
Anti-settling agent (Tyxatrol-SR)	12,4 g
Solvesso™	36,0 g

Curing took place during 40 sec. to a PMT of approximately 240°C.

The resulting coating consisted of a uniform mono-layer covering approximately 90% of the total substrate.

As to the thickness of the layers mentioned in the above examples, it should be noted that they may vary within the frame of the invention as defined in the claims. Thus, the layers may have a thickness which is greater or smaller than what is mentioned to obtain the same results.

According to present invention a retro-reflecting sheet material having excellent retro-reflective properties is disclosed. Further, the present invention discloses an efficient method of preparing said retro-reflecting sheet material by using rollers and preferably by means of coil coating. Thus, substantially all the different types of layers necessary for providing the invented retro-reflecting sheet material are applied by rollers,

and steps like the one disclosed in the prior art for applying a mono layer of glass beads and indenting beads to the surface of the substrate are superfluously. Additionally, the method for preparing the retro-reflective surface according to the invention involves proper process control, especially with regard to application of spherical beads.

Claims

1. A method of preparing a light retro-reflective surface on a substrate comprising providing several layers including a mono layer of basically spherical beads and possibly one or more transparent layers on a substrate,
characterized in that the layers are applied one by one to the substrate substantially by rollers, and between every roller application of a new layer, curing and cooling is performed.

2. A method according to claim 1,
characterized in that said layers are applied one by one to the substrate by means of coil coating.

3. A method according to claim 1 and 2,
characterized in that the mono layer of spherical beads are applied by dispersing spherical beads in a polymer coating and thereafter applying the dispersion by rollers.

4. A method according to claim 3,
characterized in that each spherical bead is coated by a transparent polymer coating and/or a light reflecting material before being dispersed in a polymer coating.

5. A method according to claim 4,
characterized in that the light reflecting material on the surface of the spherical beads is partly removed (mechanically, chemically or thermally) before applying a new layer or finishing of the retro-reflective surface.

6. A method according to claim 1,
characterized in applying a transparent upper layer by means of polymeric foil.

7. A method according to claim 1,
characterized in applying a transparent upper layer by means of powder coating.

8. A light retro-reflecting sheet material comprising a substrate made of metal, polymer or other applicable materials where said retro-reflective surface comprises several layers including a mono layer of spherical beads,
characterized in that said retro-reflective surface further comprising a layer of light reflecting material, and that substantially all said layers constituting said retro-reflective surface have been applied to the substrate by rollers.

9. A light retro-reflecting sheet material according to claim 8,
characterized in that the retro-reflective surface comprises one or more transparent layers.

10. A light retro-reflecting sheet material according to claim 8,
characterized in that the substrate is made of aluminium or an aluminium alloy.

11. A light retro-reflecting sheet material according to claim 8,
characterized in that the substrate is embossed before application of spherical, transparent beads.

12. A light retro-reflecting sheet material according to claim 8,
characterized in that each spherical bead making said mono layer is coated with a transparent material and/or light reflecting material.

13. A light retro-reflecting sheet material according to claim 8 and 12,
characterized in that the light reflecting material is a metallic coating.

14. A light retro-reflecting sheet material according to claim 8,
characterized in that the upper layer of the retro-reflective surface comprises a polymeric foil.

15. A light retro-reflecting sheet material according to claim 8,
characterized in that the upper layer of the retro-reflective surface comprises a powder coating.

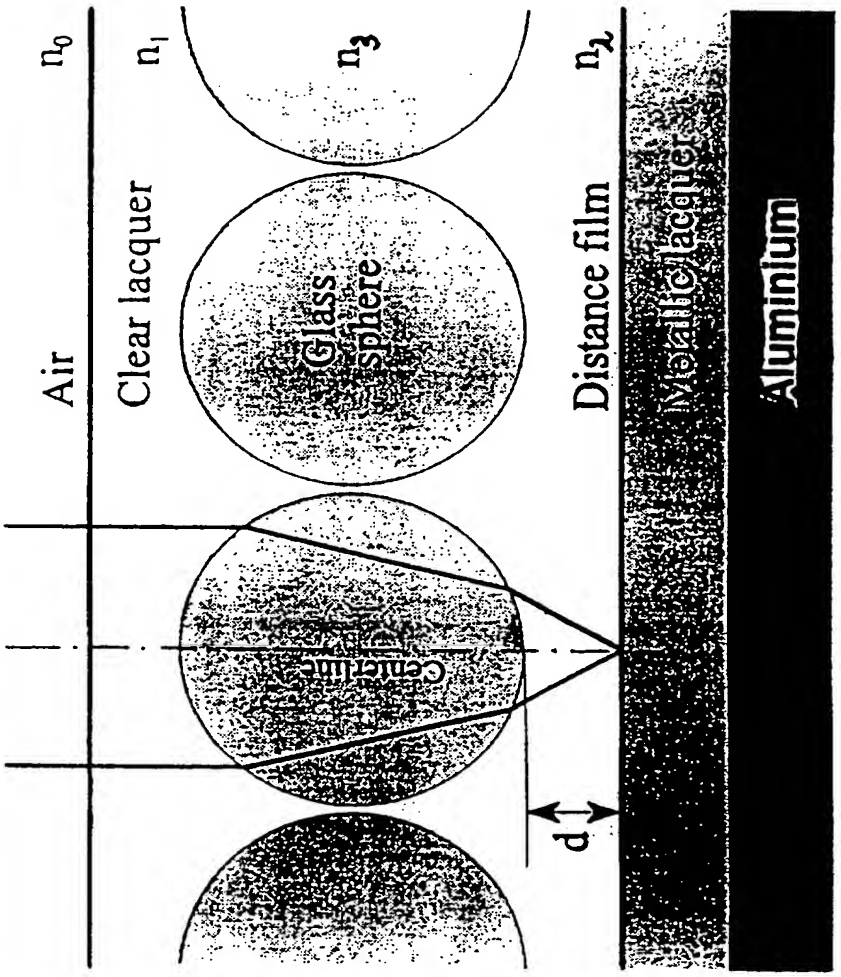
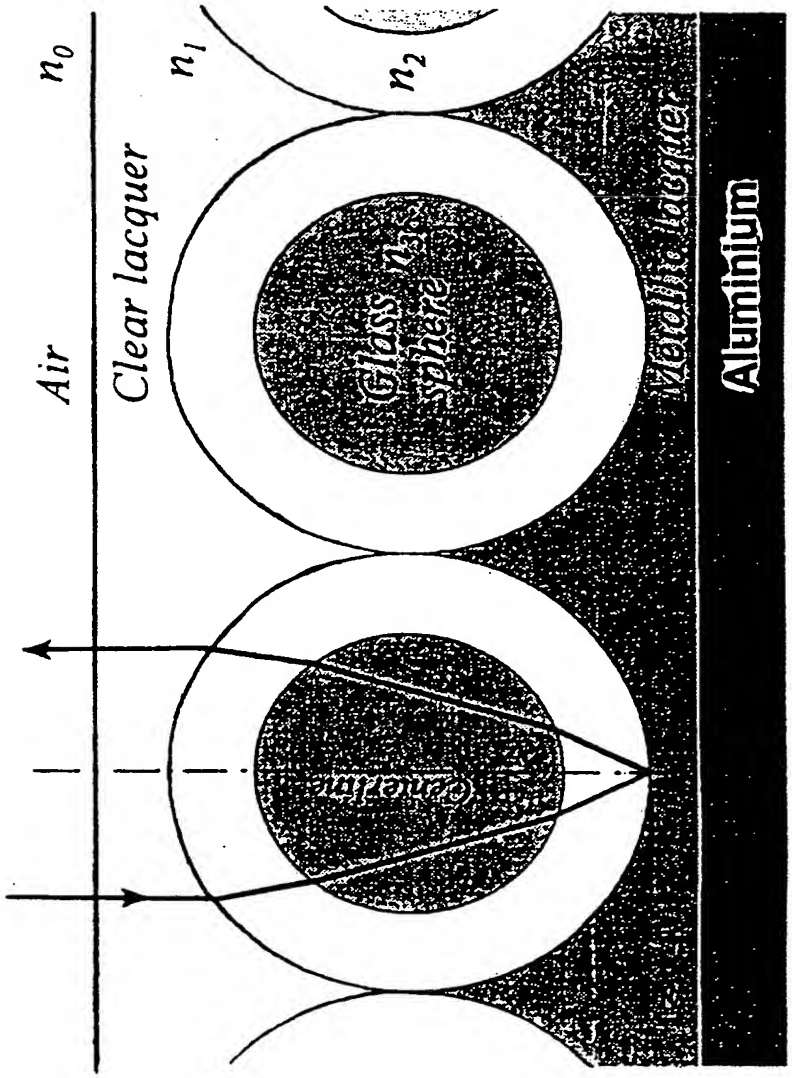

n_0
n_1
n_3
n_2
Air
Clear lacquer
Glass sphere
Distance film
Metallic lacquer
Aluminium
d

Fig. 1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Metallic lacquer
Aluminium

Fig. 2

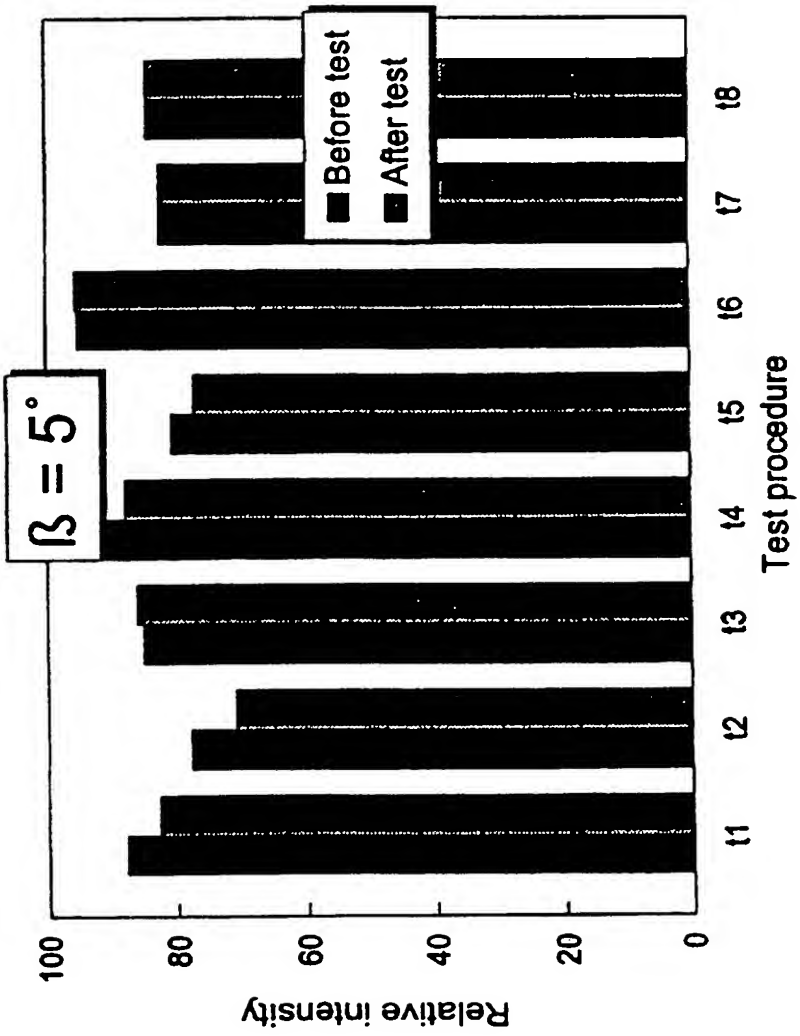
Relative intensity
100
80
60
40
20
0
t1
t2
t3
t4
t5
t6
t7
t8
Test procedure
Before test
After test
β = 5°

Fig. 3

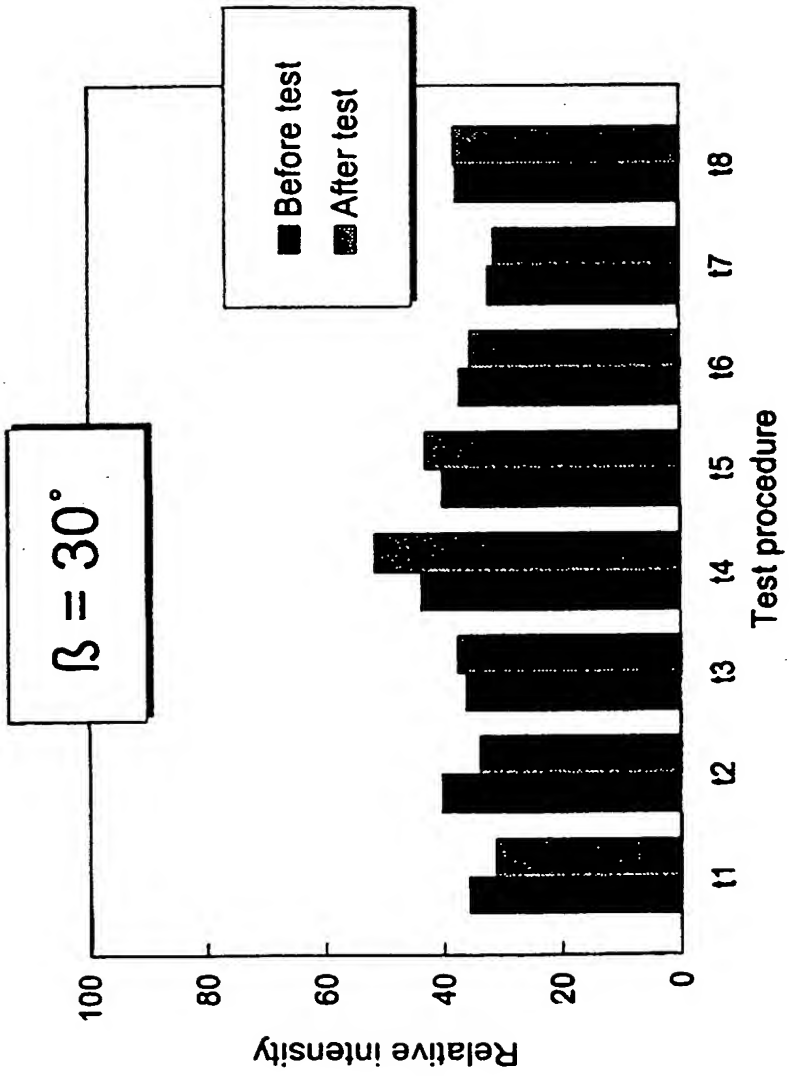

Fig. 4

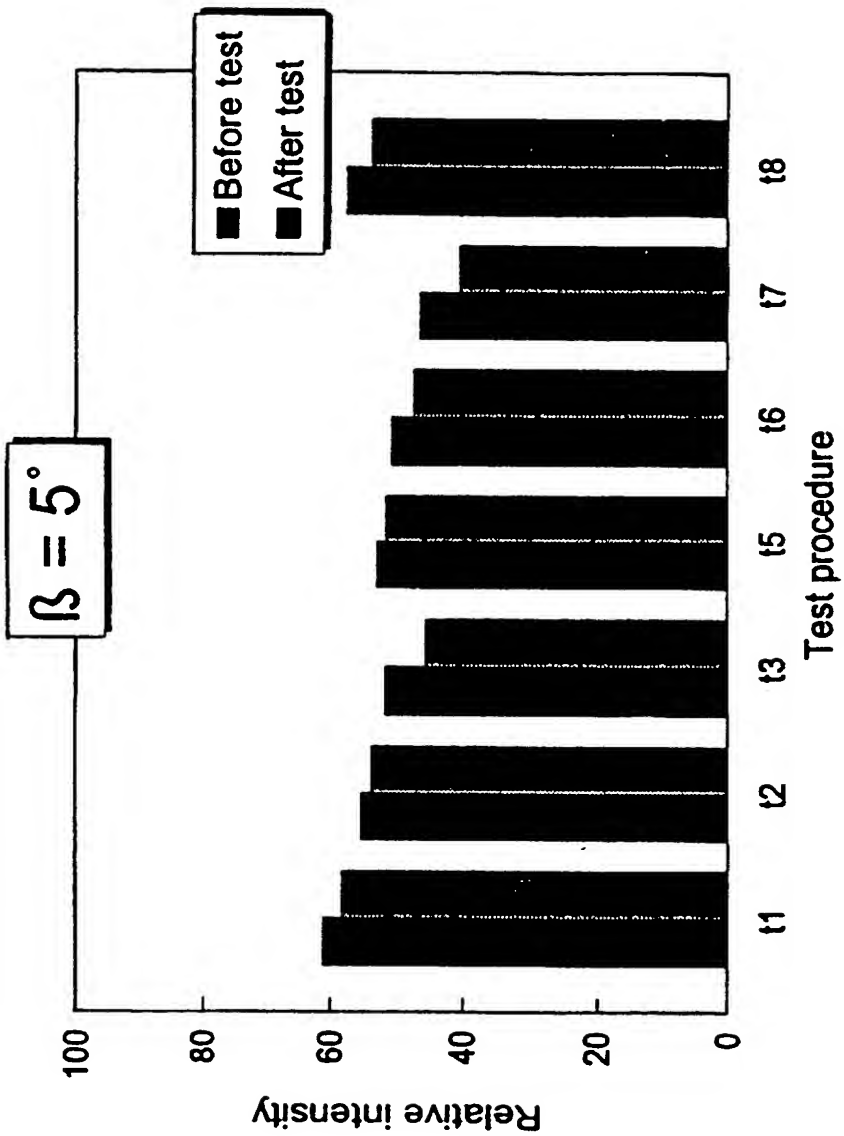
β = 5°
Before test
After test
Relative intensity
0
20
40
60
80
100
t1
t2
t3
t5
t6
t7
t8
Test procedure

Fig. 5

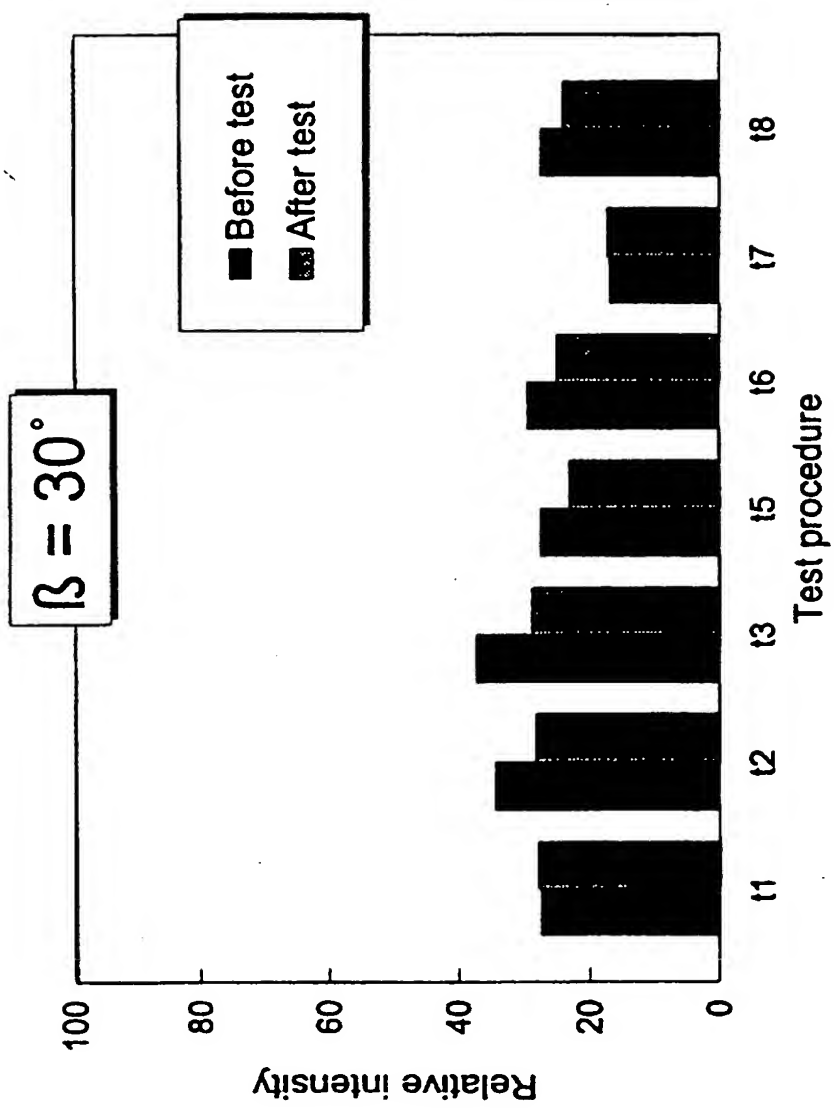
β = 30°
Before test
After test
Relative intensity
0
20
40
60
80
100
t1
t2
t3
t5
t6
t7
t8
Test procedure

Fig. 6

INTERNATIONAL SEARCH REPORT

International application No.
PCT/NO 96/00299

A. CLASSIFICATION OF SUBJECT MATTER

IPC6: G02B 5/128
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC6: B29D, G02B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPODOC, WPI, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	GB 2171335 A (SWINTEX LIMITED (UNITED KINGDOM)), 28 August 1986 (28.08.86), column 1, line 62 - column 2, line 1; column 2, line 78 - line 100	1-15
Y	JP 61171569 A (AZUMA PUREKOOTO KK), 2 August 1986 (02.08.86), abstract	1-15
A	WO 9314423 A1 (LEUCADIA, INC.), 22 July 1993 (22.07.93), page 5, line 11 - page 6, line 21, figure 5	1-15

[X] Further documents are listed in the continuation of Box C. [X] See patent family annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
15 April 1997	17 -04- 1997
Name and mailing address of the ISA/ Swedish Patent Office Box 5055, S-102 42 STOCKHOLM Facsimile No. +46 8 666 02 86	Authorized officer Johann Rigler Telephone No. +46 8 782 25 00

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INTERNATIONAL SEARCH REPORT

International application No.
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C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4265938 A (STANTON E. JACK ET AL), 5 May 1981 (05.05.81), column 4, line 63 - column 5, line 11, abstract -- --------	1-15

INTERNATIONAL SEARCH REPORT
Information on patent family members

04/03/97

International application No.
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Patent document cited in search report	Publication date	Patent family member(s)	Publication date
GB 2171335 A	28/08/86	NONE	
JP 61171569 A	02/08/86	JP 1682713 C	31/07/92
		JP 3047908 B	22/07/91
WO 9314423 A1	22/07/93	EP 0623224 A	09/11/94
US 4265938 A	05/05/81	AU 525826 B	02/12/82
		AU 5098779 A	27/03/80
		EP 0009253 A,B	02/04/80
		SE 0009253 T3	
		JP 1417008 C	22/12/87
		JP 55044899 A	29/03/80
		JP 62009023 B	26/02/87
		US 4340273 A	20/07/82